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**APPLICATION  
FOR  
UNITED STATES LETTERS PATENT**

TITLE:

PRE-ALLOYED STABILIZED ZIRCONIA POWDER  
AND IMPROVED THERMAL BARRIER COATING

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PRE-ALLOYED STABILIZED ZIRCONIA POWDER  
AND IMPROVED THERMAL BARRIER COATING

CROSS-REFERENCE(S) TO RELATED APPLICATIONS:

The present invention claims priority under 35 U.S.C. § 119 to provisional application Serial No. 60/2254,383, entitled "Pre-Alloyed YSZ powder" and filed on December 8, 2000. The entire contents of this application are hereby expressly incorporated by reference.

FIELD OF THE INVENTION

The present invention relates to the use of pre-alloyed stabilized zirconia, such as yttria-zirconia, as a raw material to form spray dried powders for use in thermal spray applications of thermal barrier coatings (TBC's) and high temperature abrasives.

BACKGROUND OF THE INVENTION

Thermal barrier coatings of alloyed yttria stabilized zirconia are used for many applications in modern turbine engines. A preferred method of producing the TBC is by thermal spraying a yttria + zirconia powder of the proper composition in order to produce a coating of the necessary composition, microstructure, and phase structure. Such powders are generally referred to as YSZ powders. The conventionally preferred types of powders used are spray-dried powders agglomerated from separate particles of yttria and zirconia which are then densified by

high temperature processing or powders formed by fusing yttria and zirconia and then crushing the alloyed material.

Spray drying is a well-known method of powder agglomeration used to produce food and pharmaceutical products in addition to thermal spray (TS) powders. The key attributes of spray dried products for the TS industry are that they are spherical, have a higher surface area compared to fused and crushed powders, and have low density. This results in powders that offer the benefits of being free flowing and that melt well within conventional thermal spray equipment.

Typically, as in the case of stabilized ceramics for TBC applications, fine particles (such as those having an average particle size of less than about 10 microns) of yttria and zirconia are mixed in water with organic binders and suspension agents to form a slurry. This slurry is then spray dried to create agglomerated particles that can then be applied using various thermal spray techniques to coat an object. A shortcoming in the use of separate yttria and zirconia raw materials is that it may result in a chemical inhomogeneity of the powder particles. Even though the bulk concentration of the starting slurry may be correct, various factors such as relative particle size distributions, mixing methods, settling, and spray drying methods, among others, may lead to non-uniform distribution of the constituents in the spray-dried particles

In order to achieve phase stability, the final coating must contain an alloy of yttria and zirconia. In the case of spray-dry powders, the alloying takes place during the process of thermal spraying or by additional processing of the powder after spray drying but before thermal spraying.

Alloying during the spraying process can be accomplished by applying the powder using a high-temperature thermal spray gun, such as a plasma gun, to ensure that the powder is melted



significant cost to the production of the powder and this processing step is still subject to the inconsistencies in the distribution of the individual particles from the spray-drying. As a result, such powders may still produce coatings with inconsistent properties.

As an alternative to spray-dried and pre-processed powders, fused and crushed powders have been used in the area of thermal spray for TBC applications. Individual yttria and zirconia powders are mixed and fused using an induction arc or other process to produce a briquette of fused material. The briquette is then crushed to produce powder of the desired size suitable for thermal spraying, generally between 11 and 150 microns.

Fused and crushed powders exhibit angular, irregular morphologies. As a result, use of these powders can cause inconsistent powder feeding. In addition, the particles are generally denser and harder to melt. This results in lower deposition efficiency due to insufficient heating of the particles in the thermal spray jet.

#### SUMMARY OF THE INVENTION

The disadvantages of known YSZ powder production techniques are addressed by the use of a pre-alloyed YSZ powder as a starting material for a spray dried powder. In particular, pre-alloyed cubic/tetragonal yttria-zirconia can be used as the starting raw material for a thermal spray powder produced by spray drying. In a preferred embodiment, pre-alloyed 8% yttria stabilized zirconia is used as a starting material. The yttria can be within a range of 5-25%. In alternative embodiments, various other pre-alloyed ceramics can be used to produce powders suitable for use in both TBC's and abradable coatings. For example, ceria, magnesia, ytterbia, scandia, dysprosia, neodymia, and calcia can replace or supplement the yttria.



DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S):

A prealloyed YSZ powder for use in spray application of thermal coatings is produced by first alloying zirconia with a stabilizer such as yttria, grinding, milling, or otherwise processing the material to produce a very fine powder having an average particle size of about one order of magnitude smaller than the desired sized particle for use in the spray application, and then processing the alloyed powder using spray drying techniques to produce the prealloyed YSZ powder with a size range that can easily be thermal sprayed.

More specifically, zirconia is initially provided typically in powder form and is alloyed with a stabilizer. The zirconia is preferably stabilized with yttria in the range of between about 5-25% by weight, more preferably between about 6-10% and most preferably about 8%. In alternative embodiments, one or more other materials can be used to stabilize the zirconia in addition to, or in place of yttria. For example, the yttria can be replaced or supplemented by ceria, magnesia, ytterbia, scandia, dysprosia, neodymia, and calcia.

Conventional techniques can be used to alloy the zirconia with the stabilizer, such as induction arc processing. It is known to alloy zirconia with yttria and then grind the alloyed material to a particle size suitable for use in thermal spray coating applications. Typical thermal spray-coating particle sizes range from between about 11 and 150 microns. In contrast, and according to the present invention, the alloyed stabilized zirconia is processed to form a base powder having particle sizes that are much smaller than is typically used for spray applications, generally in the range of one order of magnitude smaller than desired for the thermal spray coating process. In a preferred embodiment, the alloyed powder has a particle size of less than or equal to about 10 microns.





A first thermal spray coating was produced using a conventional plasma densified powder known as a hollow spherical powder ("HOSP"). This class of powder is generally considered to produce superior coatings. The specific YSZ powder used is currently available as Sulzer Metco 204CNS. Two additional coatings were produced with a pre-alloyed YSZ powder, currently referred to as Sulzer Metco AE 8017 and produced according to the present invention. An analysis of the pre-alloyed and HOSP YSZ powders used is shown in Table 1, below:

TABLE 1:

	pre-alloyed powder (-100, +200)	Standard HOSP powder
<b>Sieve (Mesh)</b>		
+100	0.2	0.2
+120	12.5	10.2
+140	46.4	42.0
+170	80.0	72.6
+200	93.7	94.0
+230	98.8	98.7
+270	99.5	99.3
+325	99.7	99.5
-325	0.3	0.5
<b>Density (g/cm<sup>3</sup>)</b>	1.15	2.17
<b>Organic Solids (wt. %)</b>	2.96	< 0.1
<b>Chemistry (wt%)</b>		
ZrO <sub>2</sub> +HfO <sub>2</sub>	91.54	93.70
Y <sub>2</sub> O <sub>3</sub>	7.87	7.50
SiO <sub>2</sub>	0.06	0.30
TiO <sub>2</sub>	<0.01	0.03
Fe <sub>2</sub> O <sub>3</sub>	<0.01	0.02
Al <sub>2</sub> O <sub>3</sub>	<0.01	<0.01
CaO	0.01	0.01
MgO	0.07	<0.01
U + Th	<0.01	0.02
<b>Monoclinic ZrO<sub>2</sub></b>	6%	4%

As can be seen, the overall composition of the two powders is substantially the same. The major difference is that the HOSP powder has a substantially higher density, the result of the plasma densification process used to alloy the zirconia with the yttria. In contrast, the prealloyed YSZ powder is much more porous, being comprised of very small particles held together by the binder. The binder in the pre-alloyed powder also introduces organic solids which are largely absent in the HOSP powder.

The three coatings were all applied using a Sulzer Metco 9MB spray gun under N<sub>2</sub>/H<sub>2</sub> conditions. The process parameters were selected to produce a coating having a porosity of about 11%. The only difference between the pre-alloyed coating process parameters was spray distances. Pre-alloyed coating A was sprayed at a distance of 4.5 in. and pre-alloyed coating B was sprayed at a distance of 5.5 in. Two distances were selected to account for possible differences in porosity. The three coatings were then cross-sectioned and polished for analysis.

Microphotographs of cross sections for the HOSP coating, pre-alloyed coating A, and pre-alloyed coating B along with porosity measurements are shown in Figs. 1-3. Each microphotograph shows the various splat boundaries and pores in the sample. While the aggregate porosity levels for the three coatings are similar, the morphology is different. In particular, the coatings produced with the pre-alloyed powder have more defects, such as splat boundaries, and have pores that are more evenly distributed and finer than those in the HOSP coating do. Empirically, the increase in and finer distribution of defects in the pre-alloyed coating indicates that the pre-alloyed coating has a shorter mean-free-path of lattice waves and a lower thermal conductivity relative to the HOSP coating.

The thermal conductivity of each of the three coatings was then analyzed. For accuracy, the characteristics of each coating were measured on a metal substrate and also on a freestanding

shape. Prior to testing, the freestanding samples were coated with 0.1 micrometer of gold and all samples were coated with approximately 5 micrometers of graphite. The freestanding samples were further polished to remove the lip from the edges on the substrate side and to smooth the roughness on the free side.

- 5 The specific heat and diffusivity for each sample was measured at 25, 500, and 1000 °C by the laser flash method using a Holometrix Thermaflash 2220 and the results used to determine thermal conductivity. The results of the test are shown in Table 2, below. A graph of the thermal conductivity vs. temperature is shown in Fig. 4

Table 2

## Laser Flash Thermal Conductivity Results

Sample	thickness @ 25°C (mm)	bulk density $\rho$ @ 25°C (g/cm <sup>3</sup> )	temperature (°C)	specific heat Cp (J/g-K)	diffusivity $\alpha$ (cm <sup>2</sup> /s)	conductivity $\lambda$ (W/m-K)
HOSP (free-standing)	0.443	4.81	25	0.458	0.00280	0.617
			500	0.596	0.00213	0.611
			1000	0.638	0.00176	0.540
Pre-ALLOY A (free-standing)	0.602	4.84	25	0.453	0.00216	0.473
			500	0.596	0.00144	0.416
			1000	0.634	0.00129	0.397
Pre-ALLOY B (free-standing)	0.542	4.75	25	0.457	0.00214	0.465
			500	0.598	0.00146	0.413
			1000	0.638	0.00124	0.375
Inconel 718 (substrate)	2.535	8.20	25	0.433	0.0289	10.3
			500	0.548	0.0416	18.7
			1000	0.674	0.0496	27.4
HOSP (coating on Inc718)	0.315	4.81	25	0.458	0.00289	0.635
			500	0.596	0.00202	0.578
			1000	0.638	0.00180	0.551
Pre-ALLOY A (coating on Inc718)	0.533	4.84	25	0.453	0.00219	0.480
			500	0.596	0.00148	0.428
			1000	0.634	0.00139	0.427
Pre-ALLOY B (coating on Inc718)	0.508	4.75	25	0.457	0.00224	0.486
			500	0.598	0.00151	0.429
			1000	0.638	0.00133	0.404

As confirmed by the analysis, the pre-alloyed coatings, while having the same aggregate composition and porosity as the HOSP coating, have a thermal conductivity which is approximately 20% lower than the standard YSZ material. This is a substantial performance increase which will provide better heat protection for a constant coating thickness when compared to conventional YSZ coatings or permit the same heat protection to be achieved with a thinner, and therefore less expensive, coating.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those of skill in the art that various changes in the form and details may be made therein without departing from the spirit and scope of the invention.